Chain Length Dependence of the Conformational Order in Self-Assembled Dialkylammonium Monolayers on Mica Studied with Soft X-ray Absorption

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Self-assembled alkyl chain-based monolayers on mica are important for industrial and technological processes because they can be used to organically modify inorganic substrates. The conformational structure and orientational order of the films determine how the modified substrate interacts with the environment and also determines the chemical character and stability of its surface. Using near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, we have systematically studied the conformational order in ion-exchanged dialkylammonium monolayers adsorbed on mica and how that order depends on the length of the alkyl chains. We found that the absolute number of gauche defects in the films increases with decreasing chain length.

Organic monolayer coatings can be employed to modify the surface properties of inorganic materials. The molecular order and orientation of the films are important parameters, since they determine the homogeneity, stability, and chemical properties of the modified surface. Films on mica have attracted less attention than the more widely studied thiol-gold system, despite their importance to industrial and technological processes. For alkane thiols on gold, it is known that the number of "gauche" conformations in the film — that is, conformational defects — depends on the temperature. But for alkyl chains with more than 11 carbon atoms, that number is rather independent of the chain length. Results from the thiol-gold system, however, cannot simply be transferred to films on mica, since the bonding mechanism and molecular arrangements are different. In the case of ion-exchanged films on mica, the packing density in the resulting film is determined by the surface cation density of the layered silicate surface.

We prepared films of dialkylammonium cations (2Cn) with n=8-18 carbon atoms per chain on mica substrates and characterized them with NEXAFS. **Figure 1** shows spectra recorded at the carbon 1s edge at grazing and normal photon incidence (left). On the right hand side, we show the corresponding difference spectra between grazing and normal incidence.

The high anisotropy of the C-H (labeled 3) and C-C related signals (labeled 4) indicates a high degree of conformational order of the alkyl chains.

The observed anisotropy can be converted into an (average) number of gauche defects per molecule. Note that each molecule contains two alkyl chains. **Table 1** summarizes these numbers for the molecular ions investigated.

Interestingly, the absolute number of defects in these films increases with decreasing chain length. This is in contrast to the thiol-gold system. **Figure 2** illustrates this result schematically.

Dialkylammonium species films with 12 or more methylene units per chain

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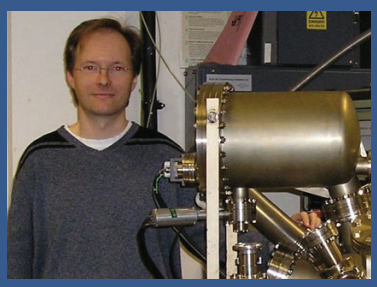

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show a significantly high degree of molecular orientation. The higher number of gauche defects found for shorter chains can be attributed to a decreasing van der Waals interaction between neighboring molecules in connection with an overall coverage of about 80%.

The employment of long alkyl chains for well ordered monolayers appears to be more important for films on mica prepared by ion-exchange compared to alkanethiols on gold. This is due to the lower overall coverage and packing density of the films on mica, which leaves more molecules exposed to uncovered regions and leads to weaker intermolecular interactions, resulting in a strong increase in the number of gauche defects for shorter alkyl chains. In order to prepare densely packed and highly ordered monomolecular films on mica, quaternary dialkyldimethylammonium ions with 16 or more carbon atoms should be employed.

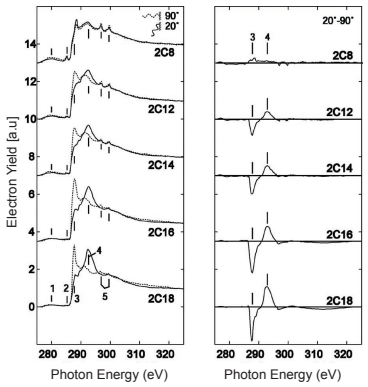

Figure 1. NEXAFS C 1s spectra of dialkyldimethylammonium films with various chain lengths adsorbed on mica recorded at normal (dashed line) and grazing (solid line) photon incidence. On the right hand side the corresponding difference spectra are shown.

	C-H	C-C
2C18	5.4(3.2)	8.3(2.5)
2C16	7.4(2.2)	11.2(1.6)
2C14	13.2(2.8)	15.4(1.4)
2C12	13.2(1.2)	15.4(1.2)
2C8	-	15.4(0.8)

Table 1. Number of gauche defects per molecule. The numbers in brackets denote the error limits.

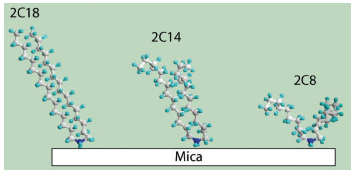

Figure 2. Schematic of the average molecular order for dialkylammonium ions of different chain length adsorbed onto mica.